

Elemental Carbon-based Method for Occupational Monitoring of Particulate Diesel Exhaust: Methodology and Exposure Issues*

The
Analyst

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Diesel exhaust has been classified a probable human carcinogen, and the National Institute for Occupational Safety and Health (NIOSH) has recommended that employers reduce workers' exposures. Because diesel exhaust is a chemically complex mixture containing thousands of compounds, some measure of exposure must be selected. Previously used methods involving gravimetry or analysis of the soluble organic fraction of diesel soot lack adequate sensitivity and selectivity for low-level determination of particulate diesel exhaust; a new analytical approach was therefore needed. In this paper, results of investigation of a thermal-optical technique for the analysis of the carbonaceous fraction of particulate diesel exhaust are discussed. With this technique, speciation of organic and elemental carbon is accomplished through temperature and atmosphere control and by an optical feature that corrects for pyrolytically generated carbon, or 'char,' which is formed during the analysis of some materials. The thermal-optical method was selected because the instrument has desirable design features not present in other carbon analysers. Although various carbon types are determined by the method, elemental carbon is the superior marker of diesel particulate matter because elemental carbon constitutes a large fraction of the particulate mass, it can be quantified at low levels and its only significant source in most workplaces is the diesel engine. Exposure-related issues and sampling methods for particulate diesel exhaust also are discussed.

Keywords: Diesel exhaust; diesel particulate; soot; carbon; carbonaceous aerosol

Introduction

The widespread use of diesel equipment has generated concern about occupational exposures to diesel engine exhaust, which has been classified as a probable human carcinogen.¹ The National Institute for Occupational Safety and Health (NIOSH) considers diesel exhaust a potential occupational carcinogen and has recommended that employers reduce workers' exposures.² This recommendation was based on results of five independent animal studies in which rats exposed to unfiltered diesel exhaust showed an increased incidence of benign and malignant lung tumours.¹ An increased incidence of lung tumours was observed in one study of mice exposed to filtered diesel exhaust, but the total incidence of lung tumours in this particular study was comparable to that for historical controls.¹

Various estimates of unit cancer risk [defined as the risk (lifetime) per unit of lifetime exposure (in $\mu\text{g m}^{-3}$)] of exposure to diesel exhaust have been calculated. In a draft quantitative risk assessment conducted by State of California Office of Environmental Health Hazard Assessment (OEHHA), carcinogenicity data from one animal bioassay³ and one human study⁴ were used to predict risks of cancer in humans exposed to ambient levels of particulate diesel exhaust. The calculated risk range based on the animal (rat) data was 3×10^{-5} – 3×10^{-4} per $\mu\text{g m}^{-3}$. Different models of carcinogenicity and different measures of exposure were used in the calculation of the range of estimates. Based on results of the human study by Garshick *et al.*⁴ and two different measures of cumulative exposure, lifetime unit risks (95% upper confidence level) of 3.4×10^{-4} and 2.3×10^{-3} were calculated. Of these two estimates, the rounded value of 3×10^{-4} was proposed as the lifetime unit risk of exposure and this value reportedly is 'consistent with the current evidence.'⁵

Particulate diesel exhaust, like particulate air pollution in general, also is of concern with respect to non-cancer health effects. The US EPA has proposed an inhalation Reference Concentration (RfC) of $5 \mu\text{g m}^{-3}$ for the non-cancer health effects of diesel exhaust,⁶ and the OEHHA has proposed to adopt this value for the chronic inhalation reference exposure level (REL) in California.⁵ The RfC for a substance is an estimate of a daily exposure of humans, including sensitive subgroups, that is 'likely to be without appreciable risk of deleterious effects during a lifetime of exposure.'⁵ A comprehensive review of the potential health effects of exposure to diesel exhaust has recently been published.⁷

Because diesel exhaust is a highly complex mixture containing thousands of compounds,^{1,2} some measure(s) of exposure must be selected. As tumour induction in animals is associated with exposure to unfiltered diesel exhaust, a measure of exposure to the particulate fraction of the exhaust was sought. Previously, specific soot-borne organic compounds have been targeted; however, this approach is limited in that selected compounds usually are present only at low (often non-detectable) levels.⁸ Further, although considerable research effort has been devoted to chemical characterization of the solvent-extractable fraction of diesel soot, a unique marker for diesel exhaust has not been found. Even if a unique marker(s) could be identified, the exhaust composition is highly variable,^{9,10} so any single compound or compound class probably would not reflect exposure to the diesel aerosol mass concentration. A review of analytical methods for chemical characterization of the organic fraction of particulate diesel exhaust has been published previously.¹¹

Gravimetric methods for diesel particulate matter have been employed for exposure monitoring. One approach¹² involves gravimetric determination of respirable combustible dust

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